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20. ABSTRACT (Continue on reverse side if necessary and identify by block number) The n-CdS flatband potential in the solid-state cell n-CdS/Nafion 117 + redox species/Au was shifted progressively in a cathode directed upon the introduction of FeCp ₂ , FeCp ₂ + Ru(bpy) ₃ ³⁺ and Ru(bpy) ₃ ³⁺ into the SPE. This cathodic shift was consistent with that for the oxidation potentials seen for Ru(bpy) ₃ ³⁺ (E ₁ = 1.25V vs SCE) and FeCp ₂ (0.285V vs SCE) in acetonitrile. Such perturbations of semi- conductor properties can be expected to form the basis of a detector technology when the semiconductor/SPE junction is exposed to selected chemical species. Originator supplied keywords include:-		

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INVESTIGATION OF PHOTOELECTRODE REDOX POLYMER JUNCTIONS

By

Ronald L. Cook and Anthony F. Sammells

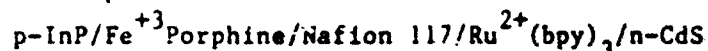
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There are several incentives for the characterization of semiconductor junctions with redox containing solid polymer electrolytes (SPE). An understanding of such junctions can be expected to have important implications on the design of solid-state photoelectrochemically rechargeable galvanic devices possessing charge capacity. In addition, the presence of polymer incorporated redox species in close proximity to the semiconductor surface may act as an antenna probe for measuring perturbations in inter-bandgap surface states when the junction is exposed to selected chemical species.

We have previously shown the viability of such junctions for the storage of photogenerated electrochemical energy.^{1,2} Here solid state cells based upon both poly(ethylene oxide) and Nafion³ as SPEs have been shown to be potentially attractive for energy storage. A recent example discussed by us is the two photoelectrode cell



which has been shown to generate photopotentials in excess of one volt upon simultaneous AM1 illumination of both photoelectrodes, using the above electrochemically reversible redox couples.² In addition, semiconductor films deposited onto appropriate substrates have been found promising, via the use of impedance techniques, for the detection of gases such as CO.⁴⁻⁶

For electrochemical energy storage, the redox polymer phase should, in principal, possess the following properties: 1) the redox species must be fixed into a relatively immobile polymer site so that any self-diffusion resulting in spontaneous self-discharge would be eliminated. 2) the immobilized redox species must retain some electrochemical reversibility and 3) an excess concentration of mobile conducting species should be present

in the vicinity of the redox couple, over and above that normally necessary for ionic conduction, to preserve electroneutrality in the proximity of the immobilized redox species during redox electrochemistry. The perfluorinated cation exchange material Nafion was selected as a candidate SPE material whose properties may address these criteria.⁷⁻¹⁰

Photoelectrochemical (PEC) cells using n-CdS as a photoanode and Nafion 117 as the SPE were prepared and doped with a variety of transition metal complexes of varying redox potentials and overall molecular charge (+2, 0, -1). The role of such introduced redox species for perturbing photoelectrode properties was of interest both for understanding conditions which promote electron transfer for charge (or discharge) in solid-state PEC storage devices, and also for understanding their role in changing semiconductor properties which might facilitate the use of this junction for various detector applications.

EXPERIMENTAL

n-CdS single crystals were obtained from Cleveland Crystals Inc. and were initially polished with 600 grit emery paper, followed by 5 micron alumina on a Texmet polishing cloth and finally with 0.3 micron alumina on a Microcloth polishing cloth. The ohmic contact area was initially etched with a solution of $\text{HNO}_3:\text{H}_2\text{SO}_4:\text{HOAc}:\text{HCl}$ (30:20:10:0.1) for 20 seconds. Ohmic contact was achieved by introduction of a gallium-indium eutectic onto the etched CdS face. Current collection was achieved via a nichrome wire using a silver epoxy, which was cured at 150°C for one hour. Immediately prior to fabrication of the cell, the front face was polished with 5 and 0.3 micron alumina, rinsed and the face etched with $\text{HNO}_3:\text{H}_2\text{SO}_4:\text{HOAc}:\text{HCl}$ solution as above.

Electrochemical measurements were performed using potentiostatic control provided by either a Stonehart Associates BC 1200 or a Wenking LT 78 potentiostat. Differential capacitance measurements for Mott-Schottky plots were performed using a HP 4276A digital LCZ meter at 1,000 and 10,000 Hz. Thin-film coatings of gold and silver were vacuum deposited on glass slides with an Edwards 306A evaporator. Photoelectrode illumination was achieved via a Sylvania 300W ELH bulb. Light intensities were measured with an Eppley 8-48 pyranometer. Cyclic voltammograms on the redox couples were run in acetonitrile (Burdick and Jackson) with tetrabutylammonium hexafluorophosphate (Southwestern Analytical Chemicals, Inc.) as supporting electrolyte. A three-electrode configuration consisting of a platinum working electrode, a platinum counter

electrode and a Ag/Ag^+ reference electrode was used for the cyclic voltammetry scans.

RESULTS AND DISCUSSION

Cell Preparation

Solid-state PEC cells were fabricated by introducing .05ml of a solution containing 50mg/ml of Nafion 117 and 0.5mg/ml of the appropriate redox couple in a solution of lower aliphatic alcohols onto the surface of n-CdS photoanode and a glass slide possessing both an evaporated gold counter electrode and silver quasi-reference electrode. The Nafion was allowed to partially dry for 15 minutes on each of these surfaces after which the two half-cells were pressed together and allowed to dry for an additional two hours. The cell configuration used in this work is shown in Figure 1. The transition metal complexes selected for introduction into the Nafion polymer included FeCp_2 , Ru(bpy)_3^{2+} , Fe(bpy)_3^{2+} , Fe(CN)_6^{4-} and Fe(acac)_3 . These complexes were selected to provide for both a variation in overall molecular charge and chemical potential at localized sites within the Nafion polymer. Several films were initially cast onto teflon substrates and allowed to dry. Upon removal and visual examination of these films (40X magnification), the polymer containing Ru(bpy)_3^{2+} was yellow in color and homogeneous. For concentrations of Ru(bpy)_3^{2+} up to 20 mg/ml SPE, the polymer remained homogeneous in appearance. Similar observations were made when Fe(bpy)_3^{2+} was introduced into the polymer.

In comparison, ferrocene, was in fact insoluble at concentrations greater than 1mg/ml of the SPE, as manifested by its appearance as microcrystalline needles upon solvent removal from the polymer. Similar observations were made when Fe(acac)_3 was introduced into the polymer. The anionic complex Fe(CN)_6^{4-} remained homogeneous at concentrations up to 2mg/ml SPE.

Photoelectrochemical Measurements

To gain some preliminary insight into the respective PEC characteristics of the SPE cell when the redox species FeCp_2 , Ru(bpy)_3^{2+} , Fe(CN)_6^{4-} and Fe(acac)_3 are present in the proximity of semiconductor/SPE junctions, cells possessing the general configuration n-CdS/SPE+redox species/Au were prepared using the procedures discussed above. The initial photopotentials realized from these cells under simulated AM1 illumination conditions are compared in Table 1. As can be seen these photopotentials (which are mainly around 200mV) appear to be relatively invariant when compared to, for example, E_1 values for the

same redox species in acetonitrile using a platinum electrode, e.g. FeCp_2 (0.285V vs Ag/Ag^+), $\text{Ru}(\text{bpy})_3^{2+/3+}$ (1.25V vs Ag/Ag^+).

Although this was initially thought explainable by the presence of Fermi level pinning by the n-CdS, it was later observed that photopotentials for $\text{Ru}(\text{bpy})_3^{2+}$ modified SPE-PEC cells were in the -500 to -600 mV range when SnO_2 conducting glass was used as the counter electrode. This result suggests that the photopotentials observed in the CdS/Nafion + Redox couple/Au system may have been limited by inadequate interfacial contact between the Nafion polymer and the gold counter electrode. Such interfacial contact limitations have previously been reported using Nafion/ WO_3 based SPE electrochromic devices.¹¹ SnO_2 , however, shows significant adhesive strength attributable to covalent bonding between the sulfonic acid groups in the SPE and receptive functional groups on the SnO_2 substrate electrode.¹² Thus the increased photopotentials observed for n-CdS/SPE cells using SnO_2 conducting glass counter electrodes can, in part, be explained by improved interfacial contact with the Nafion polymer at the counter electrode.

In order to determine the dependency of the SPE incorporated redox species concentration on the photopotential of n-CdS/Nafion + $\text{Ru}(\text{bpy})_3^{2+}$ /conducting glass, SPE cells. $\text{Ru}(\text{bpy})_3^{2+}$ concentrations were varied between .0004g and .006 g/ml/SPE and their photopotentials under $100\text{mW}/\text{cm}^2$ illumination compared. As can be seen from Table 2 the photopotentials for this system were not dependent on the concentration of the incorporated redox species over the concentration range studied, thereby indicating that the double layer present at the semiconductor/SPE junction was invariant under these experimental conditions. If significant perturbation of the double layer region were to have occurred, however, this might have influenced the photopotential observed by changing the space charge region width and the corresponding barrier height.

For cells based upon the proton conducting SPE, generally low currents were observed which were attributed to the poor conductivity of this polymer when used in solid-state cells. However, substitution of Na^+ for H^+ conductivity in the SPE/alcohol mixture before polymer formation on the semiconductor substrate was found to enhance overall ionic conductivity of the final solid-state cell. Figure 2 shows a current-voltage PEC curve for the cell n-CdS/SPE: FeCp_2 : NaCl /Au. Overall cell resistance was found to be 14K ohms and a current density of $25 \mu\text{A}/\text{cm}^2$ could be obtained by applying a 300mV

anodic overpotential to the photoanode.

Capacitance Measurements

For cells prepared in this work, differential capacitance measurements were performed on n-CdS/redox SPE junctions, to determine if there was any sensitivity of the measured n-CdS flat-band potential to the redox species introduced into the Nafion polymer. Figure 3 compares differential capacitance measurements performed on n-CdS junctions with the proton conducting SPE, (i.e., no introduced redox species) and the SPEs containing $\text{Ru}(\text{bpy})_3^{2+}$ and $\text{Ru}(\text{bpy})_3^{2+} + \text{FeCp}_2$, performed at 1,000 Hz. These C_{sc}^{-2} vs V plots show good linearity even though some of the cells possessed a relatively high resistance. Some frequency dispersion was noted at higher frequencies. Deviations from linearity for such plots might be expected if there is a high electrolyte resistance in series with the semiconductor space charge region or if a high population of surface states is present at the semiconductor/electrolyte interface.¹³ Results obtained from both current-voltage curves and the application of an AC signal to the cell, suggested that some degree of rectification may be present at the semiconductor/SPE interface. Here the AC signal from a signal generator was introduced through the cell and a measuring resistor. The output current as measured across the resistor was fed into an oscilloscope. The negative half of the sine wave was only two thirds the height of the positive half of the sine wave. This suggested that about 30% rectification was present in the cell. It should be noted that for semiconductor/metal oxide solid-state junctions where current rectification is seen, linear Mott-Schottky plots have been obtained.¹³

Since good linearity and reproducibility were obtained from C_{sc}^{-2} vs V plots in work reported here, it was of interest to compare measured n-CdS flatband potentials (V_{FB}) as a function of the introduced redox species. For the undoped proton conducting SPE, V_{FB} was +0.43V vs the silver reference electrode. Upon the introduction of $\text{Ru}(\text{bpy})_3^{2+}$ or FeCp_2 into the SPE, the n-CdS flatband potential was shifted progressively in a cathodic direction ($V_{FB} = 0.151\text{V}$, $\text{Ru}(\text{bpy})_3^{2+}$, $V_{FB} = 0.097\text{V}$, FeCp_2). This cathodic shift is consistent with that for the oxidation potentials seen for $\text{Ru}(\text{bpy})_3^{2+}$ ($E_1 = 1.25\text{V}$ vs SCE) and FeCp_2 (0.285 SCE) in acetonitrile. Similar cathodic shifts have also been observed in the cells n-TiO₂/Nafion + redox couple/SnO₂ conducting glass and n-TiO₂/polyamps¹⁴ + redox couple/SnO₂ conducting glass.

Such changes in V_{FB} may be due to modifications at the electrode surface induced either by direct adsorption of the redox couple or to variations in the capacitance associated with the polymer itself upon changing the redox species. Currently experiments are being performed by us to identify the origin of such observed V_{FB} shifts upon varying the introduced redox couple. If, in fact, the shift in V_{FB} is directly dependent in part on the redox potential of the introduced redox couple, then such semiconductor/SPE junctions might form the basis of a detector technology. For example, an introduced gas or chemical species might be expected to modify the immediate chemical environment of the SPE incorporated redox couple and thus give detectable parametric changes (e.g., V_{FB}) at the semiconductor surface.

For the n-CdS/redox SPE solid-state junctions considered here, changes occurring in the Helmholtz double layer voltage V_H as a result of varying redox species can result in perturbation of the semiconductor band-edge energy. This can be expected by consideration of the relationship:

$$V_{FB} = E_{sc}^0 - \mu + V_H$$

where μ is the difference in energy between the bulk conduction band-edge and the Fermi level, and V_H is the Helmholtz double layer voltage. When a redox-containing surface is introduced onto a semiconductor, three possibilities can be envisioned for perturbing V_H . 1) The presence of interface states at the junction may induce a voltage drop across the polymer that may be indistinguishable from a Helmholtz voltage. 2) If the polymer is insulating, the PZC (point of zero charge) will be different than that for the bare semiconductor resulting in perturbation of V_H . 3) If electron exchange can occur between semiconductor surface states and polymer incorporated redox species, then the former will define V_H and thus V_{FB} .

Donor surface states are expected near the valence band and acceptor states near the conduction band. If the E_{redox} for a redox species is below the donor state, or above the acceptor state, then the energetics will promote charging of surface states and thus change V_{FB} . Work is currently being performed directed towards clarifying which of these effects influences V_{FB} at n-CdS/SPE interface. It is not clear at this time, however, which of these mechanisms is responsible for the observed shift in the n-CdS flatband potential.

In conclusion, (1) it has been observed that the measured flatband potential in the described cells can be modified by introduction of selected redox species into the SPE (2) photopotentials in the range 500 - 600mV can be obtained if good interfacial contact is maintained at both the working and counter electrode and (3) the photopotentials obtained in the n-CdS/Nafion 117 + Ru(bpy)₃²⁺/conducting glass SPE cells are not dependent on the concentration of the incorporated redox species.

ACKNOWLEDGMENT

This work was supported in part by the Office of Naval Research.

TABLE 1

Photopotential Values for the PEC Cells CdS/Nafion + Redox Species/Au

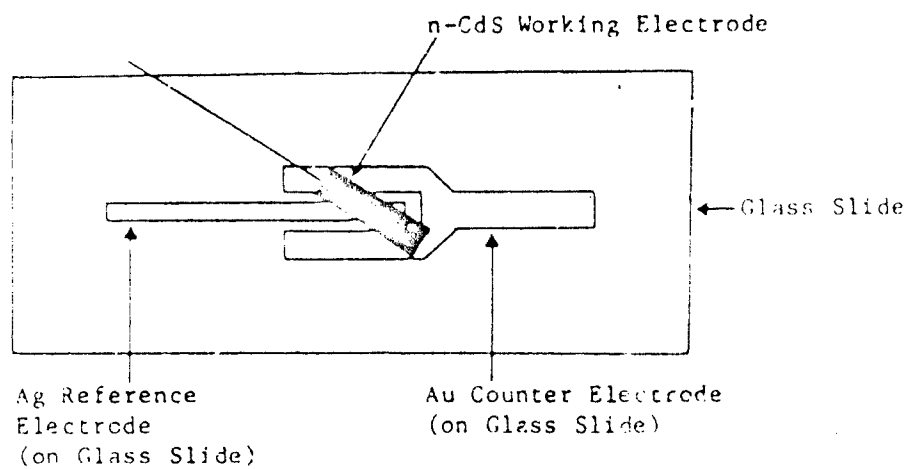
<u>Redox Species Introduced into H⁺ Conducting Nafion 117</u>	<u>Photopotential Under AM1 Illumination at n-CdS (mV)</u>
$\text{Ru}(\text{bpy})_3^{2+}$	-200
$\text{Fe}(\text{bpy})_3^{2+}$	-190
$\text{Fe}(\text{CN})_6^{4-}$	-220
FeCp_2	-270
H ⁺ Conducting Nafion	-200

TABLE 2

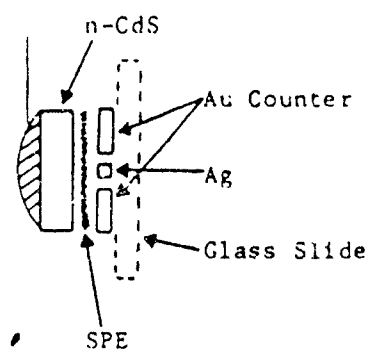
Photopotential Measurements on n -CdS/Nafion 117 + $\text{Ru}(\text{bpy})_3^{2+}$ /Conducting Glass as a Function of $\text{Ru}(\text{bpy})_3^{2+}$ Concentration

<u>$\text{Ru}(\text{bpy})_3^{2+}$ (mg/ml/SPE^a)</u>	<u>Photopotential</u>
0.375	-485
0.75	-498
1.5	-490
3.0	-480
6.3	-500

^a 1ml SPE solution contains 50mg/ml Nafion 117



TOP VIEW



SIDE VIEW

Figure 1 Schematic Diagram of Cell Configuration Used in This Work.

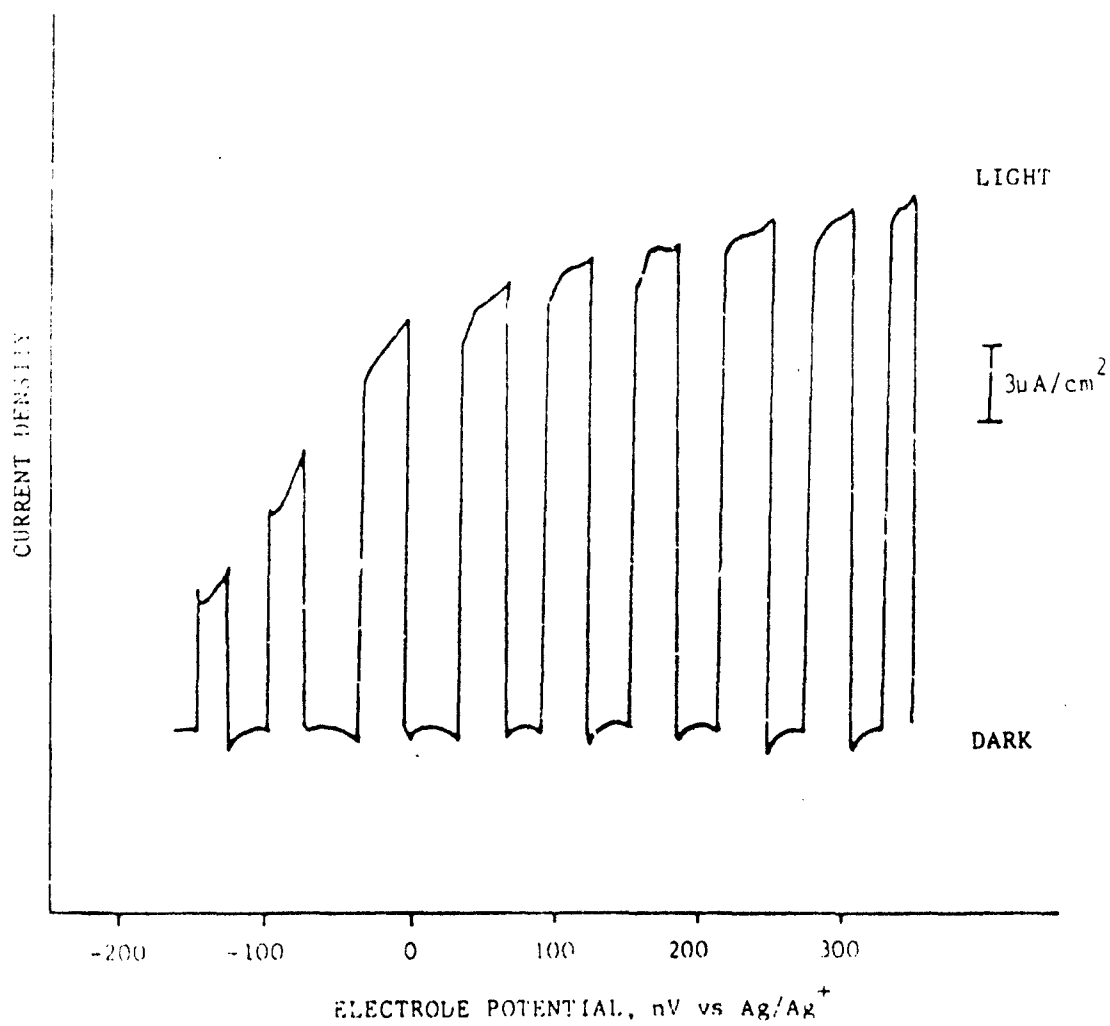


Figure 2. Current-Voltage Relationship for the Cell
n-CdS/Nafion:FeCp₂:NaCl/Au

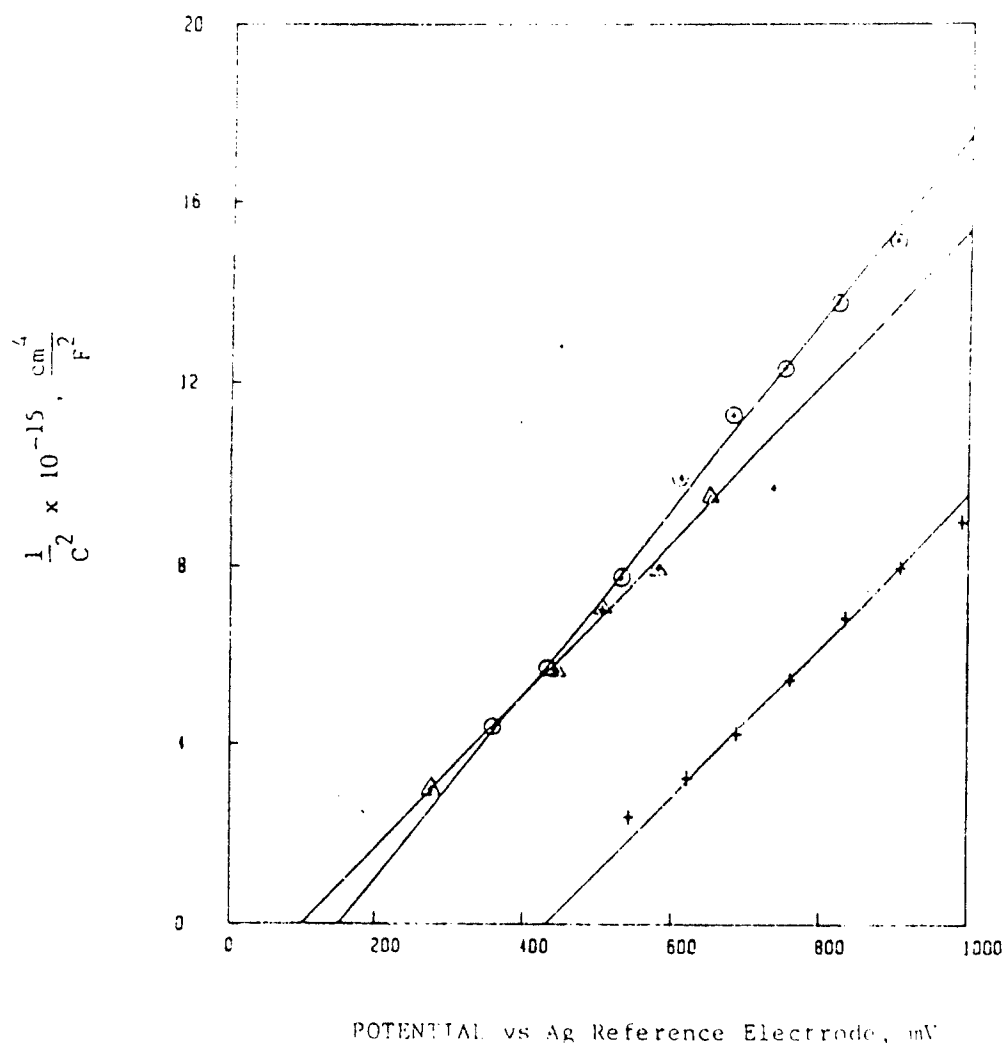


Figure 3. Mott-Schottky Plots for (+) CdS/SPE/Au, (O) CdS/SPE + Ru(bpy)₃²⁺/Au and (Δ) CdS/SPE + Ru(bpy)₃²⁺ + FeCp₂/Au.

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